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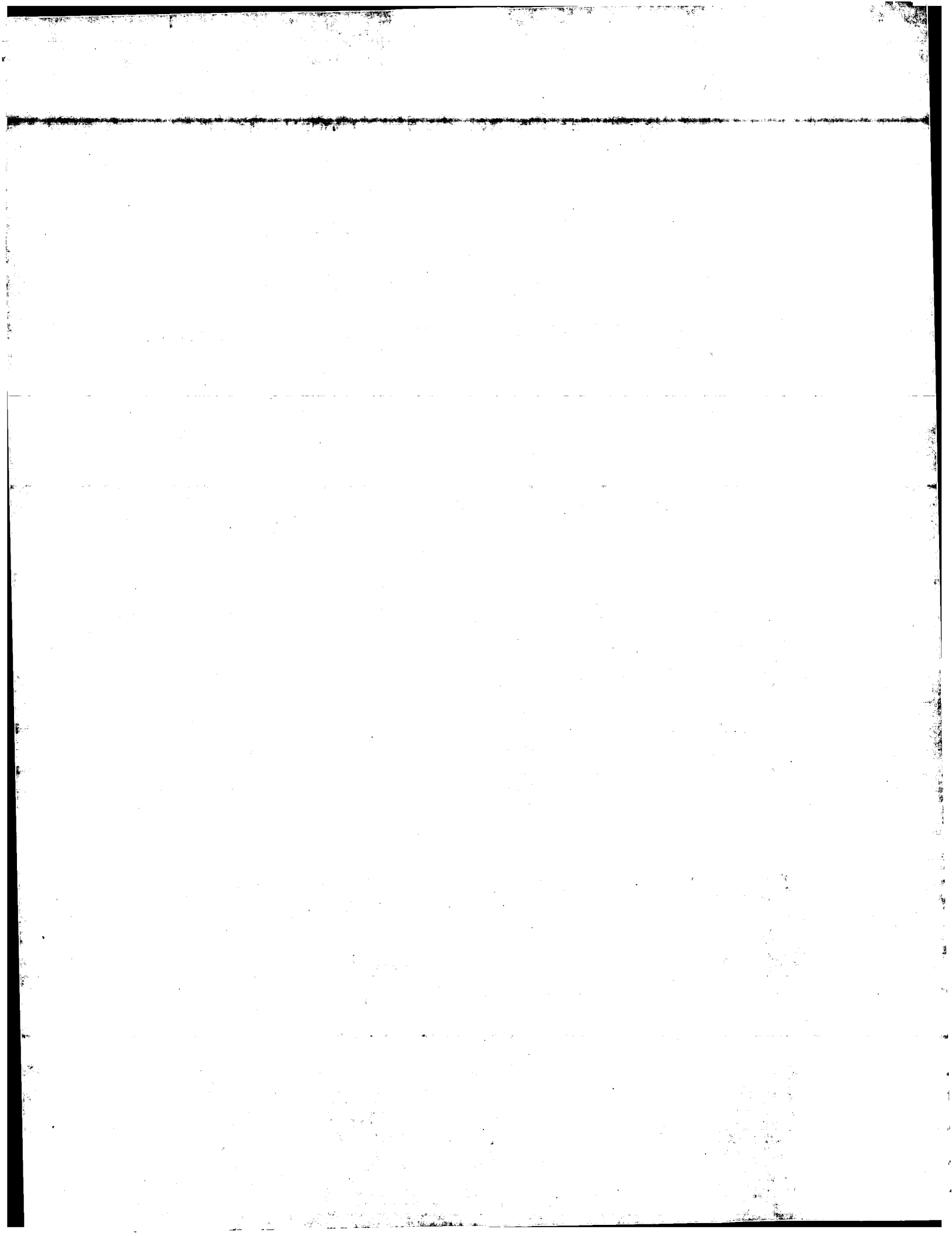
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(54) Conjugated diene rubber composition

(57) Rubber compositions having improved wet skid resistance and improved dynamic heat generating property and useful as a rubber composition for tires comprise a blend of two kinds of conjugated diene polymers having a Mooney viscosity of 20 to 120, different glass transition temperatures which fall within the range of -60°C to -20°C. and the range of -90° to -40°C., respectively, and a difference in glass transition temperature of at least 20°C., the weighted average glass transition temperature of the blend being not less than -50°C.

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SPECIFICATION

Conjugated diene rubber composition

5 The present invention relates to a conjugated diene rubber composition, and more particularly a rubber composition containing a blend of two kinds of conjugated diene polymers having a different glass transition temperature from each other. 5

Hitherto, there are known many kinds of conjugated diene polymers which are used as a component of rubber compositions. In particular, isoprene polymers and butadiene polymers synthesized by using the so-called Ziegler catalyst and butadiene polymers synthesized by using an organolithium catalyst have been manufactured as raw materials for rubber compositions on an industrial scale. These polymers are characterized by their modes of microstructure, and it is known that they are polymers having a high cis content or a high cis and trans content. It is also known that there is a close correlation between the microstructure and the glass transition temperature, and that the glass transition temperature of these polymers is within the range of -70° to -110°C. 10 15

The cured products of rubber compositions containing these polymers as a rubber component, particularly in case of applying to the use as tires for automobiles, have a feature that dynamic heat generation is a little. However, they have a drawback that the braking characteristics which are another important performance required in tires are bad, and in particular are remarkably lacking in the wet skid resistance which indicates the braking characteristic on a wet road. In order to cover up the drawback, there has been adopted, for instance, a manner using a rubber blend in which a styrene-butadiene rubber is incorporated in a suitable proportion. This manner improves the wet skid resistance, but increases the dynamic heat generation, thus resulting in increase of the rolling resistance of tires. There has not been provided a rubber composition satisfying these both characteristics together, and it is the present condition in this industry that unsatisfactory rubber compositions are used. 20 25

On the other hand, in recent years, it has been found, as disclosed in Japanese Patent Publication No. 20771/1973, that a rubber composition containing a conjugated diene polymer having a high content of 1,2-bonding provides a rubber having characteristic mechanical properties such as high impact resilience, high breaking strength and excellent low temperature resistance. Such a rubber composition is suitable as a material for tires of passenger cars, etc. In particular, it is expected that a rubber composition containing a polybutadiene having a high 1,2-bonding content would improve both characteristics of the wet skid resistance and the dynamic heat generation together. In fact, such a composition improves the both characteristics somewhat, but is not always satisfactory as a rubber composition for providing tires having a high skid resistance and a low rolling resistance which have been demanded in this industry. 30 35

In the present age where improvement of the braking characteristics or the wet skid resistance is demanded, particularly for ensuring safety with development of a superhighway system, and on the other hand, reduction of the dynamic heat generation or rolling resistance of tires is demanded due to a rise of energy cost, it is very important subject to improve the both characteristics together. 40

Accordingly, it is an object of the present invention to provide a rubber composition which can provide a rubber having a high wet skid resistance and a low rolling resistance. 45

This and other objects of the invention would be apparent from the description hereinafter.

It has now been found that when a rubber blend of two kinds of conjugated diene polymers having a specified different glass transition temperature is employed as a rubber component of a rubber composition, the wet skid resistance can be improved as compared with the use of a single conjugated diene polymer having the same degree of the glass transition temperature as the average glass transition temperature of the rubber blend, and moreover the dynamic heat generating property can be maintained on the same level. 50

In accordance with the present invention, there is provided a rubber composition comprising a blend of a conjugated diene polymer (I) and a conjugated diene polymer (II) in a ratio such that the weighted average value of the glass transition temperatures of the conjugated diene polymers (I) and (II) is not lower than -50°C., the conjugated diene polymer (I) being an amorphous polymer of a conjugated diene having a glass transition temperature of -60° to -20°C. and a Mooney viscosity ML1 + 4(121°C.) of 20 to 120, the conjugated diene polymer (II) being an amorphous polymer of a conjugated diene having a glass transition temperature of -90° to -40°C. and a Mooney viscosity ML1 + 4(121°C.) of 20 to 120, and the difference in the glass transition temperature between the conjugated diene polymers (I) and (II) being not less than 20°C. 55 60

A rubber composition containing a conjugated diene polymer having a glass transition temperature not less than -50°C. and a conjugated diene polymer having a glass transition temperature not less than -90°C. and a Mooney viscosity ML1 + 4(121°C.) of 20 to 120, and the difference in the glass transition temperature between the conjugated diene polymers (I) and (II) being not less than 20°C.

market. According to the present invention using the specified blend of conjugated diene polymers, the wet skid resistance can be further improved, and the composition of the invention is very useful as a material for tires having satisfactory both wet skid resistance and rolling resistance in practical use.

5 The conjugated diene polymers (I) and (II) used as rubber components in the present invention can be prepared by a process for the polymerization of a conjugated diene using an organic alkali metal compound as a polymerization initiator, which is known as a living anionic polymerization process. Particularly, a process using an organolithium compound as an initiator and a Lewis basic compound such as an ether or a tertiary amine as an agent for controlling the glass transition temperature of the produced polymer is preferred from the viewpoint of easiness 10 in controlling the polymerization reaction. Preferably, the polymerization is conducted in a medium. Hydrocarbons are preferably employed as a polymerization medium.

The regulation of the molecular weight of the polymers (I) and (II), namely the Mooney viscosity of the polymers, can be attained by adjusting the proportion between the monomer and the initiator used. The amount of the initiator necessary for obtaining the polymer having a Mooney viscosity of 20 to 120 is from 0.005 to 15 % by mole based on the monomer used. 15 When the Mooney viscosity of the polymers (I) and (II) is less than 20, molding of the composition is difficult because the so-called cold flowability and the strength are low, and moreover the dynamic heat generation is large and accordingly the polymers are unsuitable as a rubber component for the composition in practical use. When the Mooney viscosity of the 20 polymers (I) and (II) is more than 120, the polymers are unsuitable for practical use, because in the preparation of the composition the supply of the polymers to a processing machine is difficult and also the compoundability and dispersibility of various other additives are bad.

The glass transition temperature of a conjugated diene depends on the microstructure. The glass transition temperature of the conjugated diene polymers (I) and (II) can be regulated in a 25 known manner in which the content of microbonding, particularly the content of 1,2-bonding and/or 3,4-bonding, is regulated by the adjustment of the proportion between the Lewis basic compound and polymerization initiator used and the adjustment of the polymerization temperature. In the present invention, it is necessary that the conjugated diene polymer (I) is an amorphous polymer having a glass transition temperature of -60° to -20°C . and the conjugated 30 diene polymer (II) is an amorphous polymer having a glass transition temperature of -90° to -40°C . When the respective glass transition temperatures of the polymers (I) and (II) are lower than the above respective ranges, the effect of improving the wet skid resistance is small, and the polymers are not suitable as a rubber component of the composition. On the other hand, the 35 use of the conjugated diene polymers having a glass transition temperature higher than the above ranges is not suitable for industrial practice. Particularly, the preparation of a conjugated diene polymer having a glass transition temperature higher than -20°C . requires the use of a very large amount of the Lewis basic compound and the polymerization reaction becomes unstable. Also, a conjugated diene polymer having a glass transition temperature higher than 40 -20°C loses properties as an amorphous polymer and has properties as a resin and accordingly is unsuitable as a rubber component of the composition of the invention.

The conjugated diene polymers (I) and (II) are selected so that the difference in the glass transition temperature between them is at least 20°C . When the difference is less than 20°C ., improvement of the wet skid resistance is insufficient.

45 The mixing ratio of the conjugated diene polymers (I) and (II) is selected so that the weighted average value of the glass transition temperatures of the polymers (I) and (II) is not lower than -50°C . When the weighted average value is lower than -50°C ., the effect of improving the wet skid resistance becomes small.

Examples of the conjugated diene used for preparing the conjugated diene polymers (I) and 50 (II) are 1,3-butadiene, isoprene, 1,3-pentadiene, substituted butadienes such as 2,3-dimethyl-1,3-butadiene and 1-phenyl-1,3-butadiene, substituted 1,3-pentadienes, and the like. These conjugated dienes may be employed alone or in admixture thereof. Particularly, 1,3-butadiene or isoprene is preferably employed, because of being easily obtainable.

The rubber composition of the present invention is prepared by admixing the conjugated diene polymers (I) and (II) with usual additives such as carbon black, sulfur, a curing accelerator 55 and an antioxidant by employing a usual rubber processing machine. An extender may also be compounded, so far as the objects of the present invention are not prevented.

Preferably, the composition of the invention is prepared by previously blending the conjugated diene polymers (I) and (II), and then compounding the blend with additives such as carbon 60 black, sulfur, a curing accelerator and an antioxidant. The composition can also be prepared in such a manner as simultaneously compounding and milling the polymers (I) and (II) and additives. Also, in case of previously blending the conjugated diene polymers (I) and (II), in addition to a process of blending the polymers by a usual rubber blender, the blending may also be attained by a process in which respective polymerization reaction mixtures of the polymers (I) 65 and (II) are admixed so that the polymers are admixed in a prescribed mixing ratio, and the

polymers are separated from a solvent and recovered as a blend of the polymers (I) and (II).

The present invention is more specifically described and explained by means of the following Examples, in which all parts are by weight. These Examples are intended to illustrate the invention and are not to be understood to limit the scope of the invention. Also, it is to be

- 5 understood that various changes and modifications may be made in the invention without departing from the spirit and scope thereof. 5

Examples 1 to 3

- 10 Butadiene polymers Ia, Ib, Ic, IIa and IIb were prepared by a living anionic polymerization process employing butadiene, n-hexane as a polymerization medium, tetrahydrofuran as an agent for controlling the glass transition temperature and n-buthyllithium as a polymerization initiator in amounts shown in Table 1, respectively. The Mooney viscosity and glass transition temperature of these polymers are also shown in Table 1. 10

- 15 Compositions were prepared by employing the thus obtained polymers. The polymer Ia, Ib or Ic and the polymer IIa or IIb were admixed in a weight ratio shown in Table 2, and 100 parts of the obtained polymer blend was compounded with 60 parts of carbon black, 20 parts of linseed oil, 5 parts of zinc white, 2 parts of stearic acid, 2 parts of a curing accelerator and 1.6 parts of sulfur and was milled by 8 inch mixing rolls to give compositions. 15

- 20 The compositions were press-cured at 150°C. by employing a steam press of 150 tons to give cured products used as test pieces. The dynamic heat generation and wet skid resistance were measured. The results are shown in Table 2. 20

The physical properties of the butadiene polymers and the cured products were measured under the following conditions.

- 25 Mooney viscosity of polymer: 25

By employing a Mooney viscometer set at 121°C., a polymer was preheated for 1 minute, and after 4 minutes, the torque value was read. (ML, 1 + 4, 121°C.)

- 30 Glass transition temperature of polymer:
The measurement was made by raising the temperature from -100°C. to +20°C. at a rate of 20°C./minute employing a differential scanning calorimeter made by E.I. du Pont de Nemours & Co. The transition temperature was determined from the position of the transition heat absorption peak. 30

- 35 Wet skid resistance: 35

The wet skid resistance was measured by employing a portable skid resistance tester made by Stanley with respect to the cured rubber sheet having a thickness of 6.0 mm. An asphalt surface to which water of 20°C., was sprayed was employed as a contact road surface.

- 40 Dynamic heat generation: 40

By employing an automatic Goodrich flexometer, the measurement was made under conditions of 20 pounds in static loading, 1,800 c.p.m. in vibration, 75°C. in temperature and 0.2 inch in stroke. The temperature elevation after 14 minutes was recorded.

- 45 Comparative Examples 1 to 3 45

A rubber composition was prepared and presscured in the same manner as in Examples 1 to 3 except that the butadiene polymer Ib, Ic or IIa was employed alone as a rubber component. The results are shown in Table 2.

- 50 Comparative Example 4 50

A rubber composition was prepared and press-cured in the same manner as in Examples 1 to 3 except that commercially available styrene-butadiene rubber (SBR) (commercial name "SBR 1500" made by Sumitomo Chemical Co., Ltd.) and cis-1,4-polybutadiene rubber (cis-1,4-BR) (commercial name "JSR BR01" made by Japan Synthetic Rubber Co., Ltd.) were employed as

- 55 a rubber component. 55

The results are shown in Table 2.

Table 1

Butadiene polymer	Ia	Ib	Ic	IIa	IIb	
Polymerization formulation (part)						
5 n-Hexane	500	500	500	500	500	5
Butadiene	100	100	100	100	100	
Tetrahydrofuran	18	12	10	3	1	
n-Butyllithium	0.03	0.03	0.03	0.3	0.03	
10 Mooney viscosity						10
ML1 + 4(121°C.)	62	64	65	63	67	
Glass transition						
temperature (°C.)	-33.4	-42.8	-47.5	-62.4	-81.6	

Table 2

	Ex. 1	Com. Ex. 1	Ex. 2	Com. Ex. 2	Ex. 3	Com. Ex. 3	Com. Ex. 4	
20 Polybutadiene Ia	67	-	50	-	-	-	-	
" Ib	-	100	-	-	50	-	-	
" Ic	-	-	-	100	-	-	-	
25 " IIa	33	-	50	-	-	100	-	25
" IIb	-	-	-	-	50	-	-	
SBR	-	-	-	-	-	-	75	
Cis-1,4-BR	-	-	-	-	-	-	25	
30 Glass transition temp. of rubber component (°C.)*1	-43.0	-42.8	-47.9	-47.5	-62.2	-62.4	-70.5	30
Wet skid resistance	62	59	60	58	57	53	52	
Dynamic heat								
35 gen ration (temp. rise) (°C.)	24.3	24.5	24.0	23.7	23.4	24.1	30.2	35

(Note)*1 In case of a polymer blend, the glass transition temperature shows the weighted average value.

It is clear from Table 2 that comparing the compositions of the present invention in Examples 1 to 3 with the compositions in Comparative Examples 1 to 3 corresponding thereto respectively, the dynamic heat generating property is on the same level with those of the Comparative Examples and moreover the wet skid resistance is improved. Like this, it is clear that the composition containing as a rubber component a blend of two polybutadienes having different glass transition temperatures in a prescribed ratio is excellent in the skid resistance as compared with a composition containing as a rubber component a single polybutadiene which has a similar glass transition temperature to the weighted average glass transition temperature of the blend. Also, the composition of the present invention has far excellent characteristics that the dynamic heat generation is low and the wet skid resistance is high, as compared with a conventional rubber composition for tires as shown in Comparative Example 4. It is understood that the composition of the present invention can improve both the dynamic heat generating property and the wet skid resistance together.

In addition to the ingredients used in the Examples, other ingredients can be used in the Examples as set forth in the specification to obtain substantially the same results.

CLAIMS

1. A rubber composition comprising a blend of a conjugated diene polymer (I) and a conjugated diene polymer (II) in a ratio such that the weighted average value of the glass transition temperatures of said conjugated diene polymers (I) and (II) is not lower than -50°C., said conjugated diene polymer (I) being an amorphous polymer of a conjugated diene having a glass transition temperature of -60° to -20°C. and a Mooney viscosity ML1 + 4(121°C.) of 20 to 120, said conjugated diene polymer (II) being an amorphous polymer of a conjugated diene having a glass transition temperature of -90° to -40°C. and a Mooney viscosity ML1 + 4(121°C.) of 20 to 120, and the difference in the glass transition temperature between

said conjugated diene polymers (I) and (II) being not less than 20°C.

2. A rubber composition substantially as described with reference to the Examples.

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